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Part IV. Steam Research Program

By

Frederick G. Keyes, Leighton B. Smith, and Harold T. Gerry

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Frederick G. Keyes, Leighton B. Smith, and Harold T. Gerry

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 360)

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PART IV. STEAM RESEARCH PROGRAM[1]

BY

FREDERICK G. KEYES, LEIGHTON B. SMITH, AND HAROLD T. GERRY

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THE most comprehensive data on water vapor or steam volumes were published by Knoblauch, Linde and Klebe[2] thirty years ago. Since this publication, increased pressures and temperatures have been applied in the generation and use of steam for power until at the present time 80 atm. turbines and boilers are not uncommon and superheated steam to temperatures approaching 650° C are being considered. The insufficient range of the earlier measurements in pressure (11 atm.) and in temperature (190° C) for present day steam applications is evident, and for this reason the Steam Research Committee[3] of the American Society of Mechanical Engineers in 1921 requested the precise measurement of steam volumes to temperatures and pressures as high as modern experimental technique would permit.

The designers of boilers and steam power machines have not only used the new data as rapidly as it could be obtained from the reports presented at the annual meetings[4] of the American Society of Mechanical Engineers, but have in the past fifteen years pushed forward tentative machine designs for use at higher pressures and higher temperatures faster than exact data could be provided for definitive machine design.

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[1] The earlier papers of this series appeared as follows: Part I, Proc. Am. Acad. of Arts and Sciences, *68*, 505 (1933); Part II, ibid., *69*, 137 (1934); Part III, ibid., *69*, 285 (1934)

[2] Knoblauch, Linde and Klebe, Mittheilung über Forschungsarbeiten, Heft 21, 1905.

[3] Mech. Eng. *43*, 557 (1921).

[4] A list of these reports is given in Part I, p. 506, of the present series of papers.

At the moment the superheat temperatures of steam in actual use exceeds the upper limit of temperature (460° C) reached in the volume measurements to be reported. The range of pressure and temperature, however, over which exact measurements have been made is now so great that extrapolation to higher temperatures may be undertaken with considerable confidence. This opinion is amply supported by the comparisons of derived quantities obtained from the extrapolated volume data with similar measured quantities* obtained by colleagues in England, in Germany and in Czechoslovakia.

The economic importance of reliable steam data for engineering purposes is evident. The purely scientific importance of exact data on the properties of water is no less evident, for without extensive data no finally satisfactory correlations of important properties of aqueous solutions and other physico-chemical phenomena can be made. The data should therefore prove especially valuable in interpreting solubility effects at higher temperatures, a region of great practical significance on account of the role water plays in many geological phenomena.

The new data is of use also in connection with the development of the theory of molecular forces; a knowledge of which is of the most fundamental importance in correlating such diverse properties of matter as the departure from the ideal gas laws, viscosity, surface tension, adsorption properties, phase transformation, density dependance of dielectric constants and chemical interaction under pressure. Water consists of molecules possessing a permanent dipole and in consequence the molecular field is more complicated in its dependance on the distance of separation of the molecules than, for example, the atoms of the rare gases, hydrogen, oxygen, carbon dioxide,—gases which do not possess permanent dipoles. At the present time, p, v, T data for dipole gases is not abundant and besides ammonia there is very little data over an extended range of temperature.

The present measurements of steam volumes at various pressures and temperatures have been obtained by the methods and procedures described in Part I of the Steam Program Series of papers. The data have been presented, as obtained during the past decade, at the annual December meetings of the Steam Research Committee but neither in detail nor accompanied by an adequate discussion of their probable precision. Often also, the data for introducing certain corrections had not been obtained at the time of the

* Privately communicated.

annual reports and moreover important improvements were introduced in subsequent measurements which modified the numbers given in the running series of progress reports. In the present paper all the data taken have been reduced from the original measurements introducing every refinement possible in correcting the results for container dilation with temperature and pressure, for gauge "constant" drift with time, for volumnometer irregularities, for gauge weight calibrations, for the effects of thermometry errors, and for other effects connected with the peculiarities of the measuring procedures.

Many samples of water were used in several types of container constructed of different materials. The larger specific volumes were confined with mercury which limited the temperature to which the measurements could be carried due to the present lack of knowledge of the properties of mercury and mercury-water gas phase mixtures. On the other hand, measurements at lower temperatures and necessarily low pressures, are affected by adsorption to such an extent that below 190° C the attempt to continue the use of the static method of measurement was abandoned in favor of a new method.

Of course the older measurements of Knoblauch, Linde and Klebe are in the range below 190° C and were obtained by using a static method, thus making confirmation by an independent method especially desirable. Two modifications of the static method have been used above 190° C in the work upon which the present paper is based; and the development of a new method was undertaken in the autumn of 1929, whereby the departure of steam from the ideal gas laws could be measured directly with the fluid in a state of steady motion.[5] Adsorption under conditions of steady motion of the steam has no disturbing influence whatever on the measurements of interest. The method was first tested by using ammonia and carbon dioxide, fluids for which accurate low pressure p-v-T data are available for comparison purposes.

The new method[6,7] was applied to steam in 1933 and 1934, and supplied sufficient data to permit the correlation of steam volumes over the lower range of temperature. Since June 1934 the entire apparatus has been redesigned to give results of greater precision and useful for a greater range of temperature and pressure. In a later paper a detailed account of the apparatus will be given together with a com-

[5] See Part I, footnote 38, p. 543.

[6] F. G. Keyes and S. C. Collins, Proc. Nat. Acad. Sci. *18*, 328 (1932).

[7] F. G. Keyes and L. B. Smith, Mech. Eng. *55*, 114 (1933).

prehensive series of measurements of $\left(\frac{\partial H}{\partial p}\right)_T$ and the Joule-Thomson effect for steam, both of which may be obtained simultaneously in the same apparatus if desired.

The temperature scale employed in the measurements has already been referred to in Part I, Section 5, and is that of the platinum electrical resistance thermometer interpreted by means of the Callendar difference formula. The relation of the thermodynamic scale of temperature to the International scale[8] is of evident importance and since the writing of paper, Part I, several scores of observations of the relation of the nitrogen gas scale to the international platinum scale have been carried out in this laboratory by our colleague, Professor James A. Beattie and his collaborators. In addition, exhaustive investigations of the important fixed point, the boiling point of sulphur, have reached a stage where publication may soon be expected. The precision of the steam data secured at M.I.T. and by our colleagues is sufficiently great to make the difference between the International Kelvin scale and the thermodynamic scale deduced from the gas scale readings of great interest. The nature of the results of the M. I. T. thermometric studies emphasizes moreover the importance of independent investigations which will give precision to the calculation and comparison of derived and measured thermodynamic quantities. Certainly it now seems improbable that a final decision regarding the thermodynamic consistancy of the existing mass of steam data will be reached until the relation of the present international scale and the thermodynamic scale is known to within possibly 0.01° C over the temperature range of the measurements. The latter quantity appears to be about the order of magnitude of the reproducibility attained in the practice of thermometry by the workers in the different laboratories cooperating in the steam investigation.

The Volume Data for Steam

In Table II of paper Part I the several types of container used were listed along with their internal volumes and the coefficients of thermal expansion. The smaller specific volumes were measured by confining the water sample with the liquid phase, Fig. 9 Part I. In using this method the chief inaccuracy arises in the location of the meniscus between the vapor phase and liquid phase in the container capillary just above the surface of the molten salt bath. This uncertainty is small, the less the steam pressure relative to the saturation pressure.

[8] Burgess, U. S. Bur. of Stand. Jour. of Research, *23*, 635 (1928).

Near saturation it was necessary to wait for long periods before an equilibrium was attained, but the final perfection of the capillary cooler-heater (Fig. 10 Part I) made it possible to locate accurately the two phase miniscus, thereby expediting the measurements and increasing the precision of measurement. The device made it possible to make measurements within a small fraction of an atmosphere of the saturation pressure and in this way virtually observe directly the volume of the saturation state.

The measurements by the static method were made by observing the pressures and temperatures corresponding to a selected constant volume. The constant volume lines for any fluid are nearly linear on the t, p plane, and in determining the true saturation volume the isometrics were extrapolated both graphically and analytically, to find the temperatures corresponding to the saturation pressures. A test of the correctness of the saturation volumes may be obtained through the Clapeyron relation comparing the computed heats of evaporation with similar quantities measured by our colleagues at the U. S. Bureau of Standards. The only uncertainty in these comparisons arises from our imperfect knowledge of the relation of the indications of the platinum resistance thermometer to the thermodynamic scale.

The data obtained in the nickel container, No. 1,[9] are not reported in the present paper. These data while consistant to nearly one part in three thousand for two separate samples of water did not prove to be consistant with similar measurements made in stainless steel. No entirely satisfactory explanation of the discrepancy has been found but evidence was obtained indicating that a slow decomposition takes place with water in contact with nickel whereby nickel oxide is formed and the hydrogen completely absorbed by the metal. Our knowledge of the rate of this phenomenon is not definite and it does not appear finally satisfactory to assign all the discrepancy to the interaction. Whatever the complete account of the difficulty may be, the older measurements are certainly not in accord with repeated measurements in stainless steel in two forms of container using the water-confining and mercury-confining method.

Most of the data given in Table I have been reported in the December A. S. M. E. meetings but the numbers will be found to differ somewhat therefrom. These differences arise from a recomputation of all the directly observed data and the application of various corrections which could not be applied for lack of data at the time of the interim

[9] L. B. Smith and F. G. Keyes, Mech. Eng. *53*, 125 (1931).

reports. One of the most important of the corrections is the drift of the pressure gauge "constants" with time; an effect long suspected but not definitely settled until rather late in the steam program.* Duplicate measurements were made using different containers and varying total loadings of water, and this together with variations in general conditions provides a test of reproducibility. The absolute accuracy of the data may be judged by employing the data to derive thermodynamic quantities which may be compared with directly measured quantities. We refer particularly to comparisons of latent heats computed by means of the Clapeyron relation, values of the enthalpy, the specific heats and Joule-Thomson effect values.

The Analytical Formulation of the Data

A formulation of the data was recently published[10] and in the spring and summer of 1934 a reformulation was carried out[11] resulting in a somewhat better representation of the data. In the second formulation fewer constants (9 in place of 12) were used and a simpler equation in the form $v = f(p, T)$ was developed valid to 10 cc. per gram on the vapor saturation line. It would be desirable to have available an analytical representation to the smallest volumes but thus far it has not been found possible to develop a single equation satisfactory for the entire range from infinite volumes to, say 2 cc. per gram. It is possible without great difficulty to represent a greater range of the data when the pressure is represented as an explicit function of the volume and temperature.

The equation of state of a real gas at low pressures may be very satisfactorily derived on a rational basis when the value of the intramolecular potential is known.[12] In the case of a substance such as water composed of molecules possessing a permanent dipole, the molecular field is much more complicated[13] as compared with nonpolar molecules of which the rare gases hydrogen, nitrogen and carbon dioxide are examples. However there is enough evidence indicating that the potential corresponding to the attractive forces is very large compared to the potential of the repulsive forces in the case of the

* About 1930.

[10] F. G. Keyes, L. B. Smith and H. T. Gerry, Mech. Eng. *56*, 87 (1934).

[11] F. G. Keyes, L. B. Smith and H. T. Gerry, Mech. Eng. *57*, 164 (1935).

[12] R. H. Fowler, "Statistical Mechanics," 1929, Chap. 8. F. G. Keyes, Chem. Rev., *6*, 175 (1929). J. G. Kirkwood and F. G. Keyes, Phys. Rev., *37*, 832 (1931).

[13] J. G. Kirkwood, J. Chem. Phys. *1*, 597 (1933).

water molecule. This makes it possible to employ as a sufficient approximation the van der Waals molecular model where the potential of the repulsive forces is assumed to be infinite on molecular contact. Actually, of course, our knowledge of molecular structure has progressed sufficiently to make clear that the older concept of definite and sharp molecular boundaries has lost meaning. The approximation attending the assumption of infinite repulsive potential is however, for equation of state purposes increasingly better as the attractive potential becomes larger. The facts can be illustrated by reference to Figure 1, where the true course of the potential, V, as a function of the distance, r, is represented by the full line, while the dotted line represents conditions on the assumption that at distance σ an infinite positive or repulsive potential is encountered. It is clear that the larger the area inclosed between the negative potential curve and the r axis, the better the approximation will be for van der Waals' assumption regarding molecular forces, since the ratio of the shaded area to the whole area becomes small. Helium, hydrogen, neon offer examples of substances where the attractive potential is very small relative to the repulsive potential and the error introduced by van der Waals' assumption is far too great to be ignored. In these cases a more general form of potential must be used as for example that which sufficed very well in the case of helium where $V = c\,e^{-ar} - br^{-6}$.[14] The simple expression $V = C_1 r^{-14} - br^{-6}$ is also reasonably successful in representing the behavior of helium and hydrogen.

To derive the equation of state it is convenient to use the phase integral of Gibbs.[16] For the case of a gas at not too great pressures it can be shown[17] that the equation of state may be written as follows:

$$p = \frac{RT}{v - B^\circ} \tag{1}$$

where B_o is given by the equation

$$-B^\circ = 2\pi N \int_o^\infty \left(e^{-\frac{Pot}{kT}} - 1\right) r^2\,dr \tag{2}$$

N is Avogadro's number, "Pot" represents the molecular potential and k is Boltzmann's constant. If the van der Waals assumption is

[14] Slater and Kirkwood, Phys. Rev., *37*, 682 (1931). Kirkwood and Keyes, Phys. Rev., *37*, 832 (1931).

[16] Gibbs, "Elementary Principles of Statistical Mechanics" Equation 92.

[17] F. G. Keyes, Chem, Rev. *6*, 202 (1929).

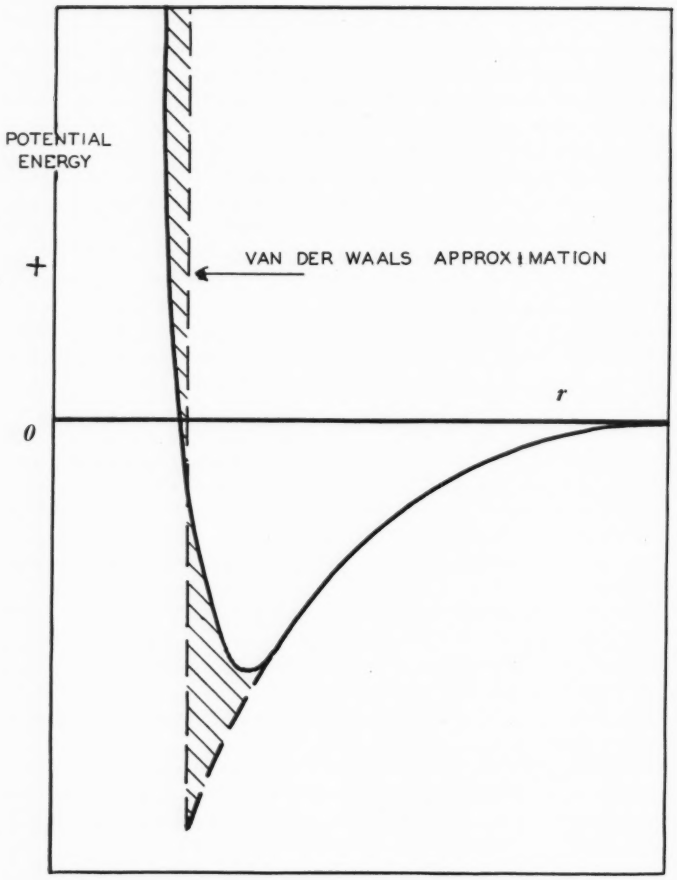

FIGURE 1

made and the attractive potential is assumed to vary as the inverse sixth power of distance[18] equation (2) may be solved and we obtain:

$$B_o = \beta - \frac{A}{RT} \sum_{j=1}^{j=\infty} \frac{1}{(2j-1)\, j!} \left(\frac{A}{RT\beta} \right)^{j-1} \tag{3}$$

where β and A are constants.

Water vapor, or steam, is composed of molecules possessing a permanent dipole and the attractive potential cannot be represented as a satisfactory approximation by a simple inverse sixth power term. The correct general expression has been recently given by Kirkwood[19] who showed that the average attractive potential consists of three terms, or rather three groups of terms. One term containing the temperature arises from the rotating dipole. There is a second term of inverse sixth power similar to that for non-polar molecules and finally a composite third term. This general potential expression by Kirkwood may be used to compute B° for water but the slow convergence of the series of terms similar to the summation in equation (3) made the use of the equation at low temperatures very inconvenient. It was found however that an empirical sum-expression could be devised which represented satisfactorily the values of B_o obtained from the measurements. The final expression obtained for B° in the case of steam is the following:

$$\frac{c.c.}{g.} B_o = 1.89 - 2641.62\, \tau\, 10^{80870\tau^2} \tag{4}$$

where τ is used to represent T^{-1}. In obtaining this equation the volume data of Table I was employed but the lowest temperature available was somewhat below 200. It is true that we have available the 1905 measurements of Knoblauch, Linde and Klebe, but these were determined by the static method which in our hands did not seem a reliable method below 190° because of adsorption of the water vapor on the walls of the container. Instead of using the K. L. and K. data, use was made of values of $\left(\frac{\Delta H}{\Delta p} \right)_T$, where H represents the en-

[18] The assumption that a simple inverse sixth power term represents the potential is of course not strictly correct. There are higher order terms, a quadrapole and even higher orders with combination terms which play an increasing rôle as the distance between molecular centers diminishes. The use of the inverse sixth power may in consequence be regarded as an approximation.

[19] J. G. Kirkwood, J. Chem. Phys. *1*, 597 (1933).

thalpy, measured directly using the "flow" method already mentioned. The values of $\left(\frac{\Delta H}{\Delta p}\right)_T$ were measured at low pressures ($\Delta p = p_2 - p_1$), and can be accurately represented as linear functions of pressure as follows: $\left(\frac{\Delta H}{\Delta p}\right)_T = \psi_o + \frac{1}{2}\varphi_1 (p_2 + p_1)$. From the latter type of formulation values of $\psi_o = \frac{\partial B_o \tau}{\partial \tau}$ may be derived and used to extend the B_o curve. The lowest temperature for which direct experimental data are available is 60°.

The theory of the equation of state is not at a stage where a suitable expression for high pressures may be derived. Moreover the "natural" form of the equation of state comes from the theory giving p as a function of v and T, or what amounts to the same thing, B as a function of v and T, whereas convenience in computing many thermodynamic quantities requires that v be given explicitly in terms of p and T. The most suitable procedure at present appears therefore to attempt to represent B in equation (1) as $B = B_o + \varphi_1 p + \ldots \varphi_n p^n$ where $\varphi_1 \ldots \varphi_n$ are temperature functions. After considerable experience accumulated in the course of numerous attempts to represent the steam data accurately, the following form for B was adopted:

$$B = B_o + \varphi_1 p + \varphi_3 p^3 + \varphi_{12} p^{12} \tag{5}$$

The first step in the process of securing the constants used to represent the temperature functions B_o, φ_1, φ_3 and φ_{12} is to obtain "B" values $\left(B = v - \frac{RT}{p}\right)$ corresponding to the pressures and volumes along isotherms. In this way a series of equations at all temperatures can be prepared by least squares as follows:

$$\begin{aligned} B_{t_1} &= B_{o_{t_1}} + \varphi_{1_{t_2}} p + \varphi_{3_{t_1}} p^3 + \varphi_{12_{t_1}} p^{12} \\ B_{t_2} &= B_{o_{t_2}} + \varphi_{1_{t_2}} p + \text{-----} \\ &\text{----------} \\ B_{t_n} &= B_{o_{t_n}} + \varphi_{1_{t_n}} p + \varphi_{3_{t_n}} p^3 + \varphi_{12_{t_n}} p^{12} \end{aligned} \tag{6}$$

To correlate the B_{o_t} terms by least square procedure, a form of temperature function was chosen in accordance with the theory already discussed. The explicit expression has already been given as equation

Container→	1B	1B	1B	1B	1B	1B	1B	1B
Vol. cc./g. → t ↓	2.0	3.0	4.0	5.0	6.25	7.5	10.0	12.5
195.0								
196.0								
197.0								
198.0								
199.0								
200.0								
210.0								
212.5								
220.0								
227.5								
230.0								
240.0								
250.0								
251.0								
260.0								
264.0								
265.0								
270.0								
280.0								
281.0								
290.0								
300.0								
305.0								
305.5								
306.0								
310.0								
313.0								
320.0								
322.0								
330.0								
332.5								130.593
340.0								135.657
344.5							151.833	
350.0							156.607	142.215
357.5						178.402		
360.0						181.389	165.137	148.566
364.5					194.118			
370.0	220.025				201.951	193.226	173.384	154.741
371.5				210.784				
375.0		220.644	219.842					
380.0	267.878	234.370	230.931	225.819	216.133	204.683	181.385	160.516
390.0	317.298	262.404	252.748					
400.0	367.654	290.947	274.367	260.715	243.518	226.821	196.909	172.435
410.0		319.801	295.536					
420.0		348.962	317.218	294.563	269.746	248.049	211.775	183.610
430.0			338.537					
440.0			359.710	327.836	295.539	268.715	226.179	194.464
460.0				360.173	320.444	288.700	240.171	204.988

TABLE I

Specific Volumes of Steam

Temperatures °C; volumes, cc./g.; pressures, International atmospheres

1B 7.5	1B 10.0	1B 12.5	1B 15.0	1B 17.5	2B 2B′ch. 20.0	2B 2B′ 20.0	1B 20.0	2B 2B′ch. 30.0	2B 2B′ 30.0	2B 2B′ 39.5	2B 2B′ 40.0	2 2′ 40.0	2B 2B′ch. 40.0	
										49.164			48.827	4
								63.730	63.622	50.322 52.008		49.856 51.533	48.996 49.855 51.511	4 5
					90.604	90.499	90.765	65.921 68.220	65.821 68.145	53.635 55.229		53.123 54.665	54.708	5
				101.287	91.143		92.582			56.745	56.192	56.169		
				104.286	96.301	96.449	96.342	72.611	72.568	58.261	57.638	57.642	57.711	5
		130.593	113.965 118.413	108.690			100.009			59.718	59.102	59.096		
		135.657	123.725	112.988	103.654	103.627	103.589	76.841	76.832				60.646	6
178.402	151.833 156.607	142.215	128.838	117.154			107.103							
181.389	165.137	148.566	133.857	121.235	110.504	110.456	110.525	80.900	80.841				63.497	6
193.226	173.384	154.741												
204.683	181.385	160.516	143.453	129.679	117.092	117.049	117.105	84.845	84.804				66.279	6
226.821	196.909	172.435	152.670	136.666	123.436	123.400	123.535	88.678	88.674				69.015	6
248.049	211.775	183.610	161.501	143.930	129.624	129.628	129.632	92.439	92.437				71.682	7
268.715	226.179	194.464	170.094	150.958	135.674	135.656	135.594	96.152	96.161				74.320	7
288.700	240.171	204.988	178.473	157.886	141.587	141.580	141.484	99.789	99.836				76.947	7

At 410° and 4 cc. the volume is evidently in error. The value 295.866 was obtained by interpolation.

2B 2B′ 40.0	2B 2B′ch. 50.0	2B 2B′ 50.0	2 2′ 57.5	2B 2B′ 75.0	2 2′ 75.0	2 2′ 97.5	2B 2B′ 100.0	2B 2B′ 140.0	2 2′ 150.0	t
								13.787		195
								13.898		196
								13.957		197
								14.003		198
								14.040		199
								14.074	13.220	200
								14.479	13.591	210
							19.612			212.5
						20.514	20.086	14.871	13.952	220
				26.238						227.5
				26.482	26.503	21.106	20.664	15.252	14.302	230
				27.303	27.309	21.688	21.217	15.627	14.647	240
	39.388	39.052	34.983	28.082	28.099	22.258	21.769	16.014	14.986	250
										251
	40.592	40.469	36.051	28.854	28.869	22.816	22.297	16.366	15.323	260
48.689										264
										265
49.753			37.090	29.592	29.618	23.365	22.825	16.745	15.658	270
51.417	43.088	42.988	38.104	30.345	30.355	23.905	23.356	17.087	15.990	280
										281
			39.101	31.055	31.081	24.437	23.863	17.448	16.319	290
54.613	45.483	45.366	40.078	31.767	31.794	24.964	24.378	17.802	16.646	300
										305
										305.5
										306
			41.035	32.476	32.496	25.485	24.881	18.146	16.971	310
										313
57.643	47.751	47.688	41.980	33.154	33.188	26.001	25.391	18.502	17.297	320
										322
			42.915	33.857	33.870	26.514	25.892	18.839	17.620	330
										332.5
60.586	49.985	49.914								340
										344.5
										350
										357.5
63.428	52.188	52.105								360
										364.5
										370
										371.5
										375
66.225	54.308	54.257								380
										390
68.963	56.426	56.384								400
										410
71.658	58.503	58.465								420
										430
74.311	60.555	60.546								440
76.966	62.608	62.605								460

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(4). Using the smoothed set of B_o values a new set of φ terms were derived using transformed equations of the form $(B - B_o)/p = \varphi_1 - \varphi_3 p^2 + \varphi_{12} p^{11}$. The φ_1 terms resulting were next correlated by least square procedure after a suitable empirical form for φ_1 had been developed. The form adopted was as follows:

$$\varphi_1 = B_o^2 g_1(\tau)\, \tau \tag{7}$$

With the smoothing function for φ_1, a set of new functions was again computed, namely $[(B - B_o)/p - \varphi_1]\, 1/p^2 = \varphi_3 + \varphi_{12} p^9$. Another set of φ_3's and φ_{12}'s was then obtained and as in the case of φ_1 a smoothing function φ_3 was developed. The form for φ_3 was the following:

$$\varphi_3 = B_o^4 g_2(\tau)\, \tau^3 \tag{8}$$

Finally, using the values of φ_3 from this smoothing function, the function $\left[\left[\frac{B - B_o}{p} - \varphi_1\right]\frac{1}{p^2} - \varphi_3\right]\frac{1}{p^9} = \varphi_{12}$ was computed. The φ_{12} values so obtained were then smoothed by determining the constants of the following form by least square computation.

$$\varphi_{12} = B_o^{13} g_3(\tau)\, \tau^{12}$$

The equation of state with the numerical values of the constants determined by least square procedure is given in full below.

$$p = \frac{4.55504\, T}{v - B};$$

$$T = (273.16 + t°C)$$

mol wt. H_2O − 18.0154
pressure in international atm.
volume in cc. per gram of steam.

$$\begin{aligned} B &= B_o + B_o^2 g_1(\tau)\, \tau p + B_o^4 g_2(\tau)\, \tau^3 p^3 - B_o^{13} g_3(\tau)\, \tau^{12} p^{12} \\ B_o &= 1.89 - 2641.62\, \tau\, 10^{80870\tau^2} \\ g_1(\tau) &= 82.546\, \tau - 1.6246\, 10^5 \tau^2 \\ g_2(\tau) &= 0.21828 - 1.2697\, 10^5 \tau^2 \\ g_3(\tau) &= 3.635\, 10^{-4} - 6.768\, 10^{64\tau^{24}} \end{aligned} \tag{9}$$

The equation is valid to 10 cc. per gram at saturation pressure and temperature but not reliable along the saturation line to smaller volumes. At higher temperatures, however, the pressures corresponding to somewhat smaller volumes may be reliable. At this point it is apropos to note that the coefficients of the pressures become

rapidly of lesser significance when higher temperatures are in question. As an example, the p^{12} coefficient at 400° C is more than 24000 times smaller than the same coefficient at 300°. The coefficient of p^3 at 400° is however somewhat less than 16 times smaller than the same coefficient at 300° while the ratio in the case of the coefficient of p is 3.56. The order of importance of the coefficients is therefore evident and it is equally evident that a very rapid simplification of the equation of state takes place as higher temperatures are approached. It is for this reason that the use of the equation for extrapolation purposes to give the volume of steam at high temperatures appears reliable provided volumes less than 10 cc. per gram are not in question.

The representation of B as a function of temperature and density is much easier than as a function of temperature and pressure. Nevertheless to represent the data to volumes as small as 3 cc. per gram has proved difficult. The selection of the simplest function consistent with precision in representing the data has not yet been made. For this reason no temperature-volume function will be given in the present paper but an equation will be given in a succeeding paper.

The Representation of the Data

Instead of tabulating the computed pressures or computed volumes using the equation of state 9 for comparison with the measured values, the following tables have been prepared giving a comprehensive survey of the degree of accord secured.

TABLE II

Deviation in Percent of Volumes Observed Less Calculated Using Equation 9. Steam Confined with Mercury

Container No.	Vol. cc./g. t	200	210	220	230	240
2	150	0.096	0.034	0.004	0.018	0.034
2B	140	.079	.001	−.031	−.027	−.009
2B	100			.142	.104	.141
2	97.5			.257	.239	.211
2B	75.0				.181	.100
2	75.0				.087	.074
2	40.0					
2B	39.5					

Average deviation 0.106 percent or one part in 940

TABLE II—continued

DEVIATION IN PERCENT OF VOLUMES OBSERVED LESS CALCULATED USING EQUATION 9. STEAM CONFINED WITH MERCURY

Container No.	250	260	270	280	290	300
2	0.064	0.082	0.093	0.105	0.121	0.137
2B	−.124	−.021	−.117	.002	−.016	−.006
2B	.129	.193	.217	.197	.260	.262
2	.192	.188	.189	.199	.217	.233
2B	.120	.100	.157	.109	.179	.204
2	.049	.041	.058	.072	.085	.110
2			−.035	−.098	−.051	.014
2B			−.014	−.029	−.010	−.007

Average deviation 0.106 percent or one part in 940

TABLE III

DEVIATION IN PERCENT OF VOLUMES OBSERVED LESS CALCULATED USING EQUATION 9. STEAM CONFINED WITH LIQUID WATER
(PARTS PER 1000 ON THE PRESSURE)

Container No.	Vol. cc./g.	260	270	280	290	300	310	320	330
2B	50	−.41		−.49		−.71		+.00	
Cap.	40		−.26	−.35		−.70		+.04	
Heater	30				−.48	−.55		−.05	
Used	20							+1.15	
1B	20						+.31	+.63	+.61
1B	17.5							+.47	+.60
1B	15.0								+.47
1B	12.5								
1B	10								
1B	7.5								

Container No.	340	350	360	370	380	400	420	440	460
2B	−.01		−.44		−.08	−.32	−.32	−.29	−.58
Cap.	+.03		.00		−.04	−.21	−.05	−.01	−.24
Heater	−.05		+.13		+.13	+.22	+.15	−.15	−.25
Used	−.28		+.03		+.18	+.40	+.27	−.04	−.33
1B	+.41	+.03	−.17		+.06	−.44	+.21	+.56	+.41
1B	+.28	+.13	−.14		−.07	−.27	+.07	+.53	+.41
1B	+.28	+.26	−.18		−.18	−.17	+.26	+.37	+.31
1B	−.18	+.05	+.05	−.02	−1.52	−.24	+.07	+.07	+.07
1B		−.74	−.52	−.18	+.14	−.01	+.11	+.02	−.02
1B			+1.16	−1.64	−1.69	−.66	+.06	−.36	−.57

Average deviation 2.64 parts per 10000

The differences between the computed and observed volumes based on an equation similar to Equation 9 but of slightly different form involving three more constants were given in Table II of Mechanical Engineering for February 1934. Since the earlier equation was published the measurements of $\left(\frac{\Delta H}{\Delta p}\right)_T$ to 60° C by Doctor Collins became available and the results were used in a re-correlation of all the steam data.

A computation of the volumes corresponding to the pressures and temperatures measured by Knoblauch, Linde and Klebe shows slightly better agreement with the observed volumes than was exhibited in Table I of the 1934 article referred to above. The present average deviation using Equation 9 for the whole range of 56 points is 0.142 percent as compared with 0.149 percent using the earlier equation. The actual numbers for six volumes are given in Table IV.

TABLE IV

DEVIATIONS OF VOLUMES OBSERVED LESS CALCULATED K. L. AND K. DATA
PARTS PER 100

Vol. cc./g.	110	120	130	140	150	160	170	180	190
1598	0.128	0.128	0.116	0.098	0.076				
1122		−.155	−.121	−.096	−.107				
740.5			.109	.113	.091	.069	.061		
389.7						−.035	−.028		
191.0								−.006	+.022

The steam for volume measurements from 150 cc. to 39.5 cc. per gram (Table II) was confined in the containers by means of mercury. Observations were taken to temperatures of 330° but subsequent comparisons with similar measurements where the steam was confined with water made clear that 330 was too high a temperature in the present stage of knowledge pertaining to the physical properties of mercury-water mixtures to permit adequate corrections to be made for the presence of mercury vapor. An important correction is of course that for the vapor pressure of mercury taking account of the effect of the pressure of the steam on the mercury (Poynting effect). The usual treatment proceeds on the assumption that the ideal gas law applies to the vapor (mercury vapor in this instance) and also that the neutral gas exerting a pressure P and the vapor of the liquid form a gaseous mixture for which Dalton's rule is valid. Neither of

these assumptions are a sufficiently close approximation[20] to enable the observed steam-mercury pressures to be corrected when the temperature exceeds 300° C.

In the case of the volume measurements where the steam was confined with water the capillary heater above the steam container facilitated measurements made near the saturation pressure. Of course the meniscus, water-steam, was greatly sharpened, but at pressures well below saturation the capillary heater does not play as important a rôle. The closer agreement between the computed volumes and those measured as shown in Table III is due in part to the fact that at higher densities adsorption effects are smaller and moreover the complications due to the presence of mercury were absent. There was also an erratic trend which has not found explanation.

Saturation Steam Volumes

A graph wherein pressure and temperature form the ordinates and abscissas will contain the saturation or vapor pressure line with the pressures and temperatures corresponding to the various constant volumes forming nearly straight lines rising from the vapor pressure curve. Each constant volume line drawn through the experimental points may be extrapolated to the vapor pressure to give the saturation pressure and temperature corresponding to the constant volume values.[21] The extrapolation would appear to offer little difficulty because the isometrics exhibit comparatively slight curvature. In the case of steam, however, and possibly the same behavior will prove true for other vapors when correspondingly precise data are available, the curvature increases perceptibly as the isometric passes into contact with the saturation pressure-temperature line.

This characteristic curvature effect in the isometrics can be made more evident by means of a special graph, Fig. 2, wherein the isometric pressures and temperatures are plotted as percentage pressure deviations from linear equations based on a pair of pressures and

[20] H. T. Gerry and L. J. Gillespie, Phys. Rev. *40*, 269 (1932) have critically considered the data for the vapor pressure of iodine obtained by the gas streaming method. In the paper cited details are given of a method for making an exact computation of the effect of a neutral gas on vapor pressure whereby the deficiencies of Dalton's rule and the ideal gas laws are avoided.

[21] A diagram of this kind will be found in Mech. Eng. *53*, 136 (1931). Fig. 1, and a preliminary set of saturation temperatures for various volumes is given in Table 4 of the same article. These values are, however, superseded by the results given in the present paper.

DEVIATION OF ISOMETRICS FROM LINEARITY

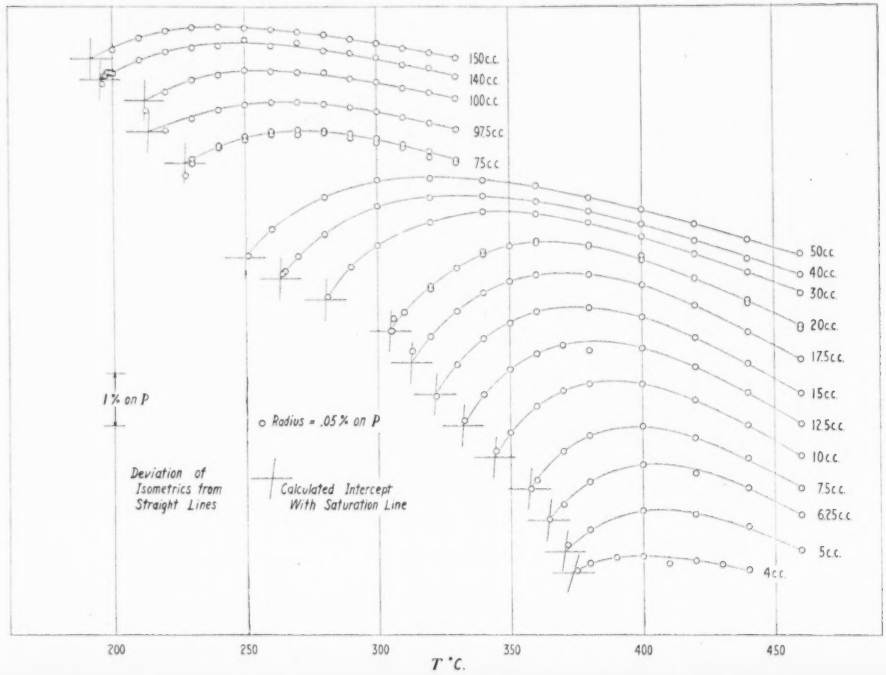

FIGURE 2

temperatures for each isometric. In the figure a different scale has been used for each isometric and the diameter of the circles corresponds in each case to a part in a thousand of the pressures. The figure makes quite evident the increased curvature of the isometric for the first 25 to 50 degrees from the saturation condition. The increased curvature appears to attain a maximum at about 10 to 20 cc. per gram and is less at 4 cc. per gram, although it must be noted that the available range of pressures and temperatures is less.

Where high precision is desired the difficulty of graphical extrapolation appears pronounced. The experience obtained thus far indicates the superiority of computing values of B ($B = v - RT/p$) from the observed data and representing them by means of a smoothing function such as, for example, the analytical expression for B in Equation 9. Once successive trials have indicated a suitable smoothing function, a least square representation of the isometric pressures and temperatures may be secured and the corresponding saturation values determined with a precision related to the suitability of the smoothing function. Table V gives a survey of the saturation volumes, column 1 of which gives the graphically extrapolated saturation temperature corresponding to the volumes of column 2. Column 3 gives the specific volume computed from the equation of state using the temperatures given in column 1 and the corresponding saturation pressures,[22] while the fourth column contains the volumes computed by means of a special equation for saturation volumes as follows:

$$v_{sat} = \frac{4.5550 \times T_s}{p_s} + B_o - \Delta B_s$$

$$\Delta B_s = \frac{1}{(0.17119 + 0.032\, x^{1/3} + 4.73 \cdot 10^{-4} x)\,(1 + 0.14 \cdot 10^{-24}\, x^{10})} \qquad (10)$$

$$x = (374.11 - t_s); \quad T_s = (273.16 + t_s); \quad B_o \text{ from Equation 9}$$

The table indicates that the saturation temperatures as determined by graphical means are in nearly all cases (isometrics for 17.5, 12.5, and 10.0 are exceptions) too low relative to the saturation temperatures that would be deduced by the equation of state using the experimental isometric volumes. The saturation temperatures obtained through the use of the equation of state are however assumed to be the more reliable in view of the apparently precise smoothing of the isometric data. To give reliable saturation volumes, the analytical method

[22] L. B. Smith, F. G. Keyes and H. T. Gerry, Proc. Am. Acad. Arts and Sci., *69*, 137 (1934). Equation (1) for vapor pressures was used.

using empirical smoothing functions requires isometric pressures and temperatures close to saturation. The steam measurements were in all cases as Fig. 2 indicates, taken as close to saturation as seemed practical and in several instances (140 cc. and 75 cc.) a number of observations were made within a fraction of a degree of the saturation temperature. A difficulty arises nevertheless since adsorption tends to its largest effect near saturation. The larger the specific volume

TABLE V

GRAPHICALLY EXTRAPOLATED ISOMETRICS AND COMPUTED SATURATION VOLUMES

t_s	Isometric vol. cc./g.	v_{1s} Eq.(9)	v_{1s} Eq.(10)
191.90	150	150.25	150.25
195.26	140	140.11	140.11
211.98	100	100.32	100.33
213.33	97.5	97.727	97.738
227.30	75	75.112	75.118
250.00	50	50.043	50.061
263.05	40	40.004	40.018
280.19	30	30.019	30.028
304.64	20	20.017	20.018
312.70	17.5	17.484	17.486
321.56	15	15.023	15.028
332.03	12.5	12.477	12.474
343.89	10	9.959	9.978
357.11	7.5	7.537*	7.502
364.05	6.25		6.253
370.53	5		4.975
373.40	4		4.127

* Saturation Volumes smaller than 10 cc. per gram are not accurately given by the Equation of state (9).

or the lower the temperature, the greater the relative importance of errors due to adsorption on the walls of the container, and the isometric pressure will tend in consequence to be low near saturation. The whole subject has been given considerable thought over a period of several years during which many variations of the graphical and analytical methods were investigated. We believe the saturation values given by the equation of state the best that can be obtained at this time with the data available.

The equation of state is valid to about 10 cc. per gram while the

special equation 10 is valid over the entire range or at least to a saturation volume of 4 cc. per gram. It is not believed however that the precision for volumes smaller than 10 cc. per gram is as satisfactory as for larger volumes. The method by which the special equation (10) was constructed is as follows:

The saturation volumes, temperatures and pressures consistent with the equation of state 9, the corresponding values from the graphical process, and the saturation pressures as given by the formula of Part II, were used to compute ΔB_s from the relation $\left(\frac{RT_s}{p_s} + B_o - v_s\right)$. The magnitude ΔB_s may evidently be represented as a function of $(374.11 - t_s)$, designated by x, or of p_s. The former independent variable was selected. By trial it was found that the reciprocal of ΔB_s tended to a limiting value as x moved to zero. The limiting value chosen was 0.17119 and the function $(\Delta B_s)^{-1} - 0.17119)\ x^{-1/3}$ appeared to vary linearly with $x^{2/3}$ when all available saturation data obtained by the graphical process were used. A straight line represented by $0.032 + 4.73 \cdot 10^{-4}\, x^{2/3}$ appeared to be satisfactory for representing the data to temperatures as low as 250° C. Comparisons were then made between the specific volumes computed with this provisional special equation and the saturation values below 200° C computed by means of the equation of state 9. From a consideration of the differences between the saturation volumes given by the provisional special equation and the saturation volumes computed from the equation of state, the term $(1 + 0.14 \times 10^{-24} x^{10})$ was devised to represent the quantity

$$[1 + (v_s \text{ provisional} - v_s)\ (0.17119 + 0.032x^{1/3} + 4.73 \times 10^{-4}x)]^{-1}.$$

The final special equation for v_s is therefore 10 above.

In Table VI the saturation volumes are given for each ten degrees from zero computed from Equation (10). Below 100° the values of the saturation volumes correspond to saturation pressures given by the following pressure-temperature relation:

$$\log_{10} p^{Int.\ Atm.} = -\frac{3142.305}{(t + 273.16)} - 8.2 \log T + 2.4804 \times 10^{-3} T + 28.5847521 \quad (11)$$

Above 100 degrees the corresponding saturation pressures are given by equation (1) of paper Part II as already stated. The formula (11) reproduces the experimental values of Scheel and Heuse more satisfactorily than formula (2) of the latter report with respect to the

TABLE VI

SATURATION VOLUMES OF STEAM COMPUTED FROM EQUATION (10) USING SATURATION PRESSURES OBTAINED FROM EQUATION (1), PART II
COMPARISONS WITH SIMILAR VOLUMES BY OSBORNE, STIMSON AND GINNINGS

t	v_s cc./g. K.S.G.	v_s cc./g. O.S.G.	t	v_s cc./g. K.S.G.	v_s cc./g. O.S.G.
0	2.0630:5	2.0643:5	200	1.2718:2	1.2716:2
10	1.0641:5	1.0650:5	210	1.0424:2	1.0425:2
20	5.7824:4	5.7872:4	220	8.6070:1	8.6060:1
30	3.2922:4	3.2942:4	230	7.1483:1	7.1470:1
40	1.9543:4	1.9550:4	240	5.9684:1	5.9674:1
50	1.2045:4	1.2047:4	250	5.0061:1	5.0054:1
60	7.6783:3	7.6788:3	260	4.2149:1	4.2145:1
70	5.0463:3	5.0464:3	270	3.5593:1	3.5593:1
80	3.4092:3	3.4094:3	280	3.0122:1	3.0124:1
90	2.3615:3	2.3617:3	290	2.5522:1	2.5527:1
100	1.6732:3	1.6733:4	300	2.1625:1	2.1634:1
110	1.2101:3	1.2103:3	310	1.8300:1	1.8312:1
120	8.9165:2	8.9179:2	320	1.5438:1	1.5454:1
130	6.6821:2	6.6831:2	330	1.2952:1	1.2968:1
140	5.0853:2	5.0861:2	340	1.0764:1	1.0776:1
150	3.9246:2	3.9250:2	350	8.802	8.798
160	3.0676:2	3.0678:2	360	6.984	6.941
170	2.4255:2	2.4256:2	270	5.093	4.949
180	1.9380:2	1.9380:2	372	4.608	
190	1.5632:2	1.5631:2	374	3.693	
			374.11	3.1975	

The digits following the numbers are the indices of 10 forming the factors by which the numbers are to be multiplied. Thus, 2.0630:5 means that the volume is 2.0630×10^5, or 206300.0 cc./g.

values from 0 to 30 degrees. It is also much simpler than Equation (5) of the earlier report, although this equation appears to be a satisfactory smoothing function over the same temperature range.

Comparisons of the present saturation volumes with those of other investigators is not easy. As a matter of fact, there has been developed only recently a method of direct measurement capable of giving highly precise values,—the general calorimetric method of Osborne, Stimson and Fioch.[23] Saturation values are of course given in the various steam tables but the most recent contain values derived from latent heats of evaporation through the Clapeyron equation. Such

[23] Osborne, Stimson and Fioch, U. S. Bur. Stand. Jour. Res. *5*, 411 (1930). Osborne, Stimson and Ginnings, Mech. Eng. *57*, 162 (1935).

values are not particularly interesting for comparison purposes without a full discussion of the sources and comparative merits of different latent heats. Moreover the most recent experimental results of our colleagues in the steam investigation are now sufficiently complete to indicate the accord between two independent methods of measurement. The Osborne, Stimson and Ginnings values given in the 1935 paper cited, extend from 0° to 370° and consist of directly measured values of $L\frac{v_1 - v_2}{v_1}$[24] designated as γ. With reliable values of dp/dT from the vapor-pressure relation v_1 is given by $\gamma/T\frac{dp}{dT}$ using the Clapeyron equation. The columns of specific volumes in Table VI headed O. S. G. were deduced from the experimentally determined γ values using the $T\frac{dp}{dT}$ values taken from the 1933 report of Osborne, Stimson, Fioch and Ginnings.[25] The agreement appears to be satisfactory to 350° and constitutes a further indication of the accord between the results of the independent investigations.[26] Our specific volumes above 350° depend on an extrapolation of saturation volumes by Equation 10 which is based on values deduced from the superheat volumes through the equation of state (9) valid to 10 cc. per gram or saturation temperatures somewhat higher than 340°. It is true that in carrying out the extrapolation the graphically deduced saturation temperatures corresponding to volumes 7.5, 6.25, 5 and 4 cc. per gram were available but the graphical extrapolation as has been suggested may not be particularly reliable and becomes more uncertain as the critical region is approached. The values due to Osborne, Stimson and Ginnings in column 3 of Table VI are considered the more reliable at 350° and higher temperatures.

Table VII contains data for the specific volumes of steam from 100° to 550° and to 400 kg./cm.^{2} computed by using equation (9) to 10 cc. per gram and for smaller volumes by graphical methods. Saturation volumes at the various temperatures are given in brackets.

[24] L represents the heat of evaporation, v_1 the saturated vapor, and v_2 the saturated liquid specific volume.

[25] Osborne, Stimson, Fioch and Ginnings, U. S. Bur. Stand. Jour. Res. *10*, 155 (1933).

[26] The Osborne, Stimson, Fioch and Ginnings values of $T\frac{dp}{dT}$ are in excellent agreement from 100 to 360° with similar values obtained by Smith, Keyes and Gerry in their Part II of the Steam Research Program. Differences for the most part are less than one in three thousand.

TABLE VII

STEAM VOLUMES IN UNITS OF 10^3 CC./G.

Kg/cm²	100°	150°	200°	250°	300°	350°	400°	450°	500°	550°
1	1.7296	1.9754	2.2158	2.4541	2.6913	2.9279	3.1641	3.4001	3.6360	3.8718
5			.4338	.4841	.5332	.5816	.6296	.6774	.7250	.7725
10			.2104	.2376	.2633	.2882	.3127	.3370	.3611	.3851
25				.08899	.1011	.1121	.1226	.1327	.1427	.1526
50					.04641	.05312	.05905	.06460	.06992	.07510
100						.02303	.02705	.03041	.03345	.03632
150						.01198	.01610	.01890	.02125	.02336
200							.01031	.01305	.01511	.01687
250							.006366	.009456	.01139	.01296
300							.003022	.006979	.008898	.01035
350							.002173	.005168	.007108	.008494
400								.003858	.005774	.007109

The Enthalpy of Steam

The enthalpy, H, may be conveniently derived by starting with the differential equation $\left(\frac{\partial H}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial v\tau}{\partial \tau}\right)_p$ where τ represents T^{-1}. Using the equation of state (9) it is evident that the right hand member becomes $\left(\frac{\partial B\tau}{\partial \tau}\right)_p$. Integration gives the following relation:

$$H = H_o + \int_o^p \left(\frac{\partial B\tau}{\partial \tau}\right)_p dp \tag{12}$$

where H_o is a pure temperature function, the nature of which is evident upon differentiating (12) with respect to temperature subject to the condition that p decreases to zero. We then find:

$$\left(\frac{\partial H_o}{\partial T}\right)_{p \to o} = C_p^\circ \tag{13}$$

where C_p° is the heat capacity steam would have at very low, in the limit zero, pressure; a pure temperature function. The equation (12) may now be written:

$$H = h_o + \int_{T_o}^T C_p^\circ \, dT + \int_o^p \left(\frac{\partial B\tau}{\partial \tau}\right)_p dp \tag{14}$$

and h_o is a constant to be determined when a condition of reference is selected.

The second term of the right hand member of (12) is readily obtained from the B form given under (9) leading to an equation which may be written as follows:

$$H = h_o + \int_{T_o}^T C_p^\circ \, dT + \frac{\partial B_o\tau}{\partial \tau} p + 1/2 \frac{\partial (B_o\tau)^2 \cdot g_1(\tau)}{\partial \tau} p_2 + 1/4 \frac{\partial (B_o\tau)^4 \cdot g_2(\tau)}{\partial \tau} p^4 - 1/13 \frac{\partial (B_o\tau)^{13} \cdot g_3(\tau)}{\partial \tau} p^{13} \tag{15}$$

The value of C_p° is evidently of great importance but unfortunately the heat capacity of a gas or vapor is very difficult to measure accurately although great ingenuity has been exercised in the attempt to secure reliable values. H. N. Davis[27] reduced 178 of the older

[27] H. N. Davis, Mech. Eng., *46*, 85 (1924).

determinations of Knoblauch and Jacob[28] by means of the Joule-Thomson data obtained by Davis and Kleinschmidt[29] obtaining values of C_p° for temperatures from 135 to 350°. The fundamental equation required for the analytical reduction is as follows:

$$C_{p_o} = C_p + \int_o^p \mu \left(\frac{\partial C_p}{\partial T}\right)_p dp + \int_o^p C_p \left(\frac{\partial \mu}{\partial T}\right)_p dp \qquad (16)$$

where C_p is the heat capacity at pressure p and μ is the Joule-Thomson coefficient. The results of the computations led to the following equation for C_p° valid from 140 to 350°.

$$C_{p\ Int.\ j.}^{\circ} = 1.7435 + 8.54 \cdot 10^{-4} t \qquad (17)$$

A reformulation of the same specific heat data including results obtained by Regnault and by Brinkworth was later undertaken by Professor J. H. Keenan[30] using additional Joule-Thomson data. The following equation resulted from the investigation:

$$C_{p\ Int.\ j.}^{\circ} = 1.4421 + 1.13 \cdot 10^{-3} t + \frac{121.4}{T} \qquad (18)$$

In a later paper Davis and Keenan[31] again discussed the specific heat data including the recent measurements of Knoblauch and Raisch[32] and Knoblauch and Koch[33] but without altering the equation (18) for C_p°.

H. Hausen[34] published a paper in 1931 in which a formula for C_p° due to Wohl and von Elbe[35] was used in a formulation of the quantity $(C_p - C_p^\circ)$. The formula[36] has a quasi-quantum theoretical basis and is given in the following form:

$$C_p^\circ = \frac{R}{18}[4 + E(x_1) + 2E(x_2)] \qquad (19)$$

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2} \quad ; \quad \begin{matrix} x_1 = \Theta_1/T; & \Theta_1 = 2280 \\ x_2 = \Theta_2/T; & \Theta_2 = 5370 \end{matrix}$$

[28] Knoblauch and Jacob, Forscharb. Berlin, Heft 35 and 36, 109 (1906).
[29] Davis and Kleinschmidt, Mech. Eng. *45*, 165 (1923).
[30] J. H. Keenan, Mech. Eng., *48*, 144 (1926).
[31] Davis and Keenan, Mech. Eng. *51*, 922 (1929).
[32] Knoblauch and Raisch, Zeit. Ver. Deutsch. Eng. *66*, 418 (1922).
[33] Knoblauch and Koch, Zeit. Ver. Deutsch. Eng. *72*, 1733 (1928).
[34] H. Hausen, Forschung auf dem Gebiete des Engeneurwesens, *2*, 319 (1931).
[35] Wohl and von Elbe, Zeit. für Phys. Chem. (B) *5*, 241 (1929).
[36] See Max Jacob's comments, Engineering, *132*, 684 (1931).

Keyes, Smith and Gerry[37] in 1934 published a formulation of the new volume data of Smith and Keyes[38] which enabled all the new specific heat data,[39] the Joule-Thomson data and the new determinations of the enthalpy of steam by Osborne, Stimson and Fioch to be used for computing C_p°, and the following equation was deduced to represent the results:

$$C_{p\ Int.\ j}^{\circ} = 1.8738 + 3.211 \times 10^{-4}t + 1.488 \times 10^{-9}t^3 \qquad (20)$$

In the meantime S. Sugawara[40] had formulated the new steam data and proposed an equation for C_p° based on his computations. His equation follows:

$$C_{p\ Int.\ j}^{\circ} = 1.9088 + 9.2931 \times 10^{-7}t^2 \qquad (21)$$

In view of the almost insuperable difficulty of measuring the low pressure heat capacities of gases with high precision, there can be little question that the most reliable method of obtaining an accurate knowledge of C_p° is through the use of band spectrum data. Until recently however[41] a satisfactory analysis of the rotation-vibration band spectrum data for water vapor had not been carried out. Some further work remains to be done but sufficient is known to permit calculation of reliable thermodynamic properties and the required computations have recently been made by A. R. Gordon[42] leading to values of the entropy and heat capacity for water vapor in the hypothetical ideal gas state. It is believed that Gordon's values, extending from 25° to 1200° are the most satisfactory existing data and these C_p° values will be used in completing the enthalpy equation. The following empirical form[43] suffices for the temperature range of interest.

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[37] Keyes, Smith and Gerry, Mech. Eng. *55*, 87 (1933).

[38] Smith and Keyes, Mech. Eng., *54*, 123 (1932).

[39] W. Koch, Forschung auf dem Gebiete des Engenieurwesens, *3*, 1 (1932).

[40] S. Sugawara, Mem. College of Eng., Kyoto Imp. Univ. *7*, 17 (1932).

[41] Mecke, Zeit. f. Physik, *81*, 313 (1933). Baumann and Mecke, Zeit. f. Physik, *81*, 445 (1933). Freudenberg and Mecke, Zeit. f. Physik, *81*, 465 (1933).

[42] A. R. Gordon, J. Chem. Phys. *2*, 65 (1934).

[43] We owe this formula to Professor J. H. Keenan. The formulation based on the Gordon values and used in computations for the Third International Steam Conference was $C_p^\circ = 1.798 + 0.00148 \dfrac{T^2}{T + 2000}$.

$$C_{p_{Int.\,j.}}^{\circ} = 1.47198 + 7.5566 \times 10^{-4}T + \frac{47.8365}{T} \qquad (22)$$

$$\int_{273.16}^{T} C_p^{\circ}\, dT = 1.47198\,(T-273.16) + 3.7783 \times 10^{-4}\,(T^2-273.16^2) + 110.14757 \log_{10} \frac{T}{273.16}$$

Table VIII gives a survey of the values of C_p° from the sources referred to above for temperatures 100, 200, 300, 400.

TABLE VIII

COMPARISON OF C_p° VALUES FROM VARIOUS SOURCES

	J. H. Keenan 1926	K.S.G. 1934	Wärmeta-			A. R.	A.R.G.
t	Eq. 18	Eq. 20	bellen	W.von E.	Sugawara	Gordon	(Keenan)
100	1.8804	1.9074		1.8844	1.9181	1.8820	1.8821
200	1.9247	1.9500	1.9333	1.9352	1.9460	1.9305	1.9306
300	1.9929	2.0106	1.9996	1.9947	1.9914	1.9887	1.9886
400	2.0745	2.0982	2.0442	2.0573	2.0575	2.0517	2.0517

We will evaluate the enthalpy constant using the enthalpy of steam, at 100° and saturation pressure, as determined by Osborne, Stimson and Fioch; our colleagues in the steam investigation. The enthalpy is recorded under the convention that the enthalpy of the liquid at zero and saturation is zero. Of course zero is the temperature of equilibrium of water, ice under a pressure of one atmosphere whereas the triple point of water is 0.01° C and should preferably be taken as the reference temperature for enthalpy and entropy. We will take for the enthalpy of saturated steam at 100° and one international atm. the quantity 2675.35 Int. joules (H_{s1}^{100}). Making use of the Gordon C_p° values as represented by Keenan's empirical formula (22) and the equation of state (9) to evaluate the remaining integral of (14), we find for h_o the number 2502.36. The equation (15) may now be written in the following abbreviated form, using A, B, C, D to represent the coefficients of pressure.

$$H_{s1}{}_{(Int.\,j.)} = 2502.36 + \int_{T_o}^{T} C_p^{\circ}\, dT + Ap + Bp^2 + Cp^4 - Dp^{13} \qquad (15A)$$

In Table IX the values of enthalpy corresponding to the saturated vapor state, H_{s1}, are tabulated from 0 to 350. In the second column the latent heats are given computed by means of the Clapeyron

TABLE IX

LATENT HEATS OF EVAPORATION AND ENTHALPY OF STEAM FOR THE SATURATED VAPOR

t	$L^{Clap.}$	$L^{O.S.G.}$	$H_{s1}{}^{Eq.\ 15A}$	$H_{s1}{}^{O.S.G.}$
0	2500.15	2497.77[a]	2501.86	2497.77[a]
10	2476.18	2475.21[a]	2520.11	2517.23[a]
20	2452.42	2452.38[a]	2538.24	2536.21[a]
30	2428.88	2429.27[a]	2556.27	2554.86[a]
40	2405.14	2405.85[a]	2574.17	2573.19[a]
50	2381.37	2382.10	2591.86	2591.21
60	2357.40	2357.97	2609.27	2608.88
70	2333.05	2333.41	2626.39	2626.16
80	2308.18	2308.36	2643.33	2643.03
90	2282.75	2282.79	2659.49	2659.44
100	2256.64	2256.59	2675.35	2675.35
110	2229.80	2229.69	2690.65	2690.67
120	2202.18	2202.05	2705 33	2705.42
130	2173.68	2173.52	2719.30	2719.45
140	2144.19	2144.02	2732.50	2732.73
150	2113.60	2113.40	2744.84	2745.14
160	2081.78	2081.61	2756.24	2756.64
170	2048.61	2048.46	2766.59	2767.11
180	2013.95	2013.83	2775.81	2776.44
190	1977.63	1977.54	2783.81	2784.53
200	1939.52	1939.44	2790.46	2791.25
210	1899.00	1899.36	2795.65	2796.51
220	1857.10	1857.07	2799.22	2800.13
230	1812.37	1812.34	2801.13	2801.98
240	1764.95	1764.92	2801.11	2801.88
250	1714.52	1714.55	2799.00	2799.69
260	1660.74	1660.85	2794.58	2795.13
270	1603.18	1603.44	2787.57	2788.00
280	1541.34	1541.83	2777.63	2777.96
290	1474.57	1475.39	2764.33	2764.64
300	1402.08	1403.33	2747.05	2747.56
310	1322.80	1324.52	2725.06	2725.99
320	1235.22	1237.33	2697.32	2698.89
330	1137.14	1139.30	2662.51	2664.69
340	1024.99	1026.35	2618.44	2620.76
350	892.15	891.12	2562.58[a]	2562.48
360	724.73	717.2	2491.27[a]	2479.9
370		438.2		2332.7

[a] Extrapolated.

All values are in Int. joules per gram of steam using the factor 1.0003 for the ratio of the absolute to the international joule. The factor used to convert cc. atm. to int. j. was 0.101295.

equation, using the values of v_1 from Table VI, dp/dT and v_2 from parts II and III of these reports.[44]

The corresponding values of latent heats and enthalpy given by Osborne, Stimson and Ginnings[45] are also listed in columns three and five. The agreement is quite satisfactory with the exception of the values above 340°. The saturation volumes above 350°, as stated in discussing Table VI, are difficult to obtain precisely by graphical extrapolation of the isometric data and the larger latent heats in column two are due to the fact that our larger volumes were used in the computation. In a later paper the isometrics for volumes smaller than 10 cc. per gram will be represented analytically thereby making it possible to carry out the extrapolation with greater precision.

Latent Heats Below Fifty Degrees

It will be noted that the enthalpy at 0° computed from the Clapeyron relation and from the H_{s1} equation differs by 1 part in 1460, a quantity that is larger than is desirable in view of the accord at higher temperatures. Unfortunately there are few data available in this region. The lowest temperature for which latent heats have been measured with modern equipment[46] is 50° where the measured value 2382.1 is to be compared with 2381.37 from column two; a difference of 1 part in 3300. The difference cannot all be due to an error in the saturation specific volume since the volume given by Osborne, Stimson and Ginnings differs by 1 part in 6000 from that used in the computation. The value of T_o (273.16) used in the present paper is probably in error at most by 1 part in 10000 relative to the true value, while the accord of the international temperature scale with the thermodynamic scale is entirely satisfactory in this region according to a private communication from Professor Beattie, who bases his opinion on many comparisons between his gas and resistance thermometers.[47] The quantity most likely in doubt is the value of $\frac{dp}{dT}$. All values of $\frac{dp}{dT}$ employed below 100° are based on the data of the Physikalisch Technische Reichsanstalt tables of 1909, and the derivatives obtained

[44] L. B. Smith and F. G. Keyes, Proc. Am. Acad. Arts and Sci. *69*, 285 (1934); *69*, 137 (1934).

[45] Osborne, Stimson and Ginnings, Mech. Eng. *57*, 162 (1935).

[46] N. S. Osborne, Mech. Eng. *53*, 137 (1931).

[47] This conclusion is also supported by the earlier work of Henning and his coworkers.

by Osborne and Myers[48] above 50° differ from the values used in the present paper (derived from equation 11) by 1 in 7400 at most. At 50° the difference is 1 in 12000, dropping to 1 in 2400 at 30° and to 1 in 650 at 0°. In part II of the steam papers some comments were made regarding the difficulty of obtaining derivatives below 50° and further comment may now be made on the basis of the H_{s1} equation from which latent heats may be derived by subtracting at corresponding temperatures the value of H_{s2} due to Osborne, Stimson and Ginnings.

To establish the equation (15A) there is available as already stated the Gordon C_p° values which we consider the most reliable available. We have also very exact measured values of the liquid enthalpy, which were used in part III to derive values of C_{p2}, the heat capacity for constant pressure for the saturated liquid. Finally there is available the equation of state (9) for steam. It proves of interest to use these data to compute the change of the latent heat with temperature and view the trend of the values below 50°. The significance of any peculiarities of trend in $\frac{dL}{dT}$ derives from the relation of the quantity to the vapor pressure, or in our case more immediately to $\frac{dp}{dT}$.

It is convenient in computing $\frac{dL}{dT}$ to use the following equation:[49]

$$\frac{dL}{dT} = C_{p1} - C_{p2} + \left[\left(\frac{\partial v_1\tau}{\partial\tau}\right)_p - \left(\frac{\partial v_2\tau}{\partial\tau}\right)_p\right]\frac{dp}{dT} \qquad (23)$$

where C_{p1} and C_{p2} are the constant pressure heat capacities at saturation pressures. Below 100° $\left(\frac{\partial v_2\tau}{\partial\tau}\right)_p$ is small relative to $\left(\frac{\partial v_1\tau}{\partial\tau}\right)_p$ (1 part in 186 at 100°)* and may be neglected. C_{p1} is given by the relation $C_{p1} = C_{p1}^\circ + \partial/\partial T \int\left(\frac{\partial v_1\tau}{\partial\tau}\right)_p dp$ and C_{p2} has already been given

[48] N. S. Osborne and C. H. Myers, U. S. Bur. of Standards J. Res. *13*, 1 (1934).

[49] This equation is a new form of a familiar equation. It is exact and may be easily derived from the relation

$$\frac{dL}{dT} = C_{p1} - C_{p2} + L/T - L/v_1 - v_2\left[\left(\frac{\partial v_1}{\partial T}\right)_p - \left(\frac{\partial v_2}{\partial T}\right)_p\right]$$

* Of course far less at lower temperatures.

(Table VIII, part III). Table X gives the computed values of $\frac{dL}{dT}$ and similar quantities derived from the Osborne, Stimson and Ginnings latent heats. From Fig. 3, prepared from the entries in Table X, it is clear that there is a maximum in the computed values at about 15°. Of course it has long been known that a minimum existed in C_{p2} below 50°, and accordingly it is to be expected that the course of the $\frac{dL}{dT}$ curve might exhibit some peculiarity of trend in approximately the same temperature range. The question of the quantitative accuracy of the computed numbers is important. The values for C_{p1} and $\left(\frac{\partial v_1\tau}{\partial \tau}\right)_p$ are computed using the equation of state 9. The values of $\frac{dp}{dT}$ used are not important since they are sufficiently exact for our present purpose. The fraction of $C_{p1}^\circ - C_{p2}$ due to the equation of state contribution is 0.02 at 0°, 0.044 at 20°, and 0.104 at 50°. It would appear therefore that the numbers should be reliable as to trend and at least approximately correct in magnitude.[50]

Clearly if a maximum exists in the $\frac{dL}{dT}$ relation there must be a corresponding inflection in L as a function of T. The inference is therefore that dp/dT will exhibit a related peculiarity in about the same region and if dL/dT could be accurately represented as a function of temperature along with $T\frac{dp}{dT}B$[51] it should be possible, in principle, to carry out the required integrations and obtain the relation between saturation pressure and temperature subject to the condition that L and p are known at 100°. In practice this has proven to be difficult owing to the large number of terms which arise. It may appear

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[50] An empirical equation representing $\frac{dL}{dT}$ is as follows:

$$\frac{dL}{dT} = \left(-2.390 + 4.038 \cdot 10^{-3} t - 1.3584 \cdot 10^{-4} t^2 + 26.6038 \frac{t^2}{T^2} - 2.3128 \cdot 10^6 \frac{t^2}{T^4} \right) I.j.$$

[51] From the Clapeyron equation and the equation of state, neglecting v_2. we find

$$T\frac{dp}{dT}(v_1 - v_2) = L = RT^2 \frac{d \log p}{dT} + T\frac{dp}{dT}B = \int \frac{dL}{dT} dT$$

TABLE X

VALUES OF $\frac{dL}{dT}$ COMPUTED USING EQUATION 23

t	$-\frac{dL}{dT}$ Eq. 23[52]	$-\frac{dL}{dT}$[53]
0	2.390	
10	2.366	
20	2.366	2.291
30	2.378	2.326
40	2.398	2.358
50	2.421	2.393
60	2.452	2.434
70	2.491	2.480
80	2.532	2.530
90	2.570	2.587
100	2.621	2.654

simpler to evaluate $\frac{dp}{dT}$ using the values for v_1 from Table VI and L from the H_{s1} equation. This procedure, however, leads to no more information and the values of v_1 are of course computed from the equation of state using pressures given by the vapor pressure equation 11 so that the $\frac{dp}{dT}$ values obtained by this calculation would not be independent of the assumed vapor pressure values.

We believe it best to postpone further consideration of this interesting subject until exact data on latent heats over the region of interest become available, and possibly also the results of a special investigation of the vapor pressures of water. Before leaving the subject it is worth noting that the successive differences in $T \log p$ for 5° intervals using the Reichsanstalt vapor pressures indicate a maximum in the differences. The numbers have been used to construct figure (4).

The discussion and intercomparison of the older body of latent heat measurements has been critically carried out by one of our colleagues

[52] The values in this column could have been derived from the H_{s1} equation 15A diminished by H_{s2}. Because of the maximum in $\frac{dL}{dT}$ it is simpler to proceed by the use of Eq. 23.

[53] Computed from the latent heats of Osborne, Stimson and Ginnings using the Rutledge method for derivatives (Phys. Rev. *40*, 262, 1932).

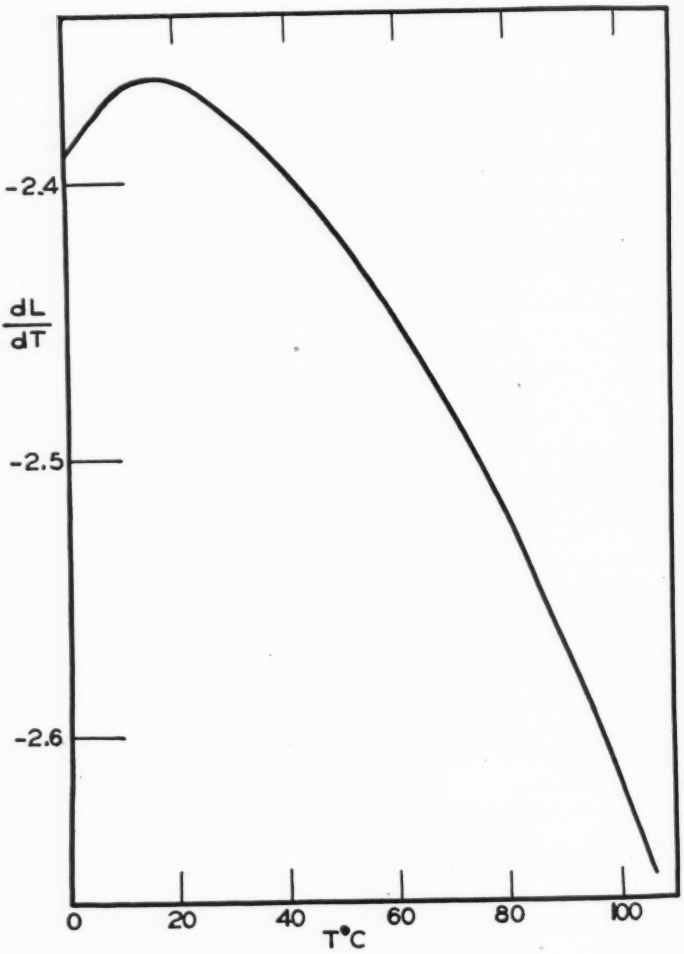

FIGURE 3

in the steam program of research in a recent publication.[54] It was shown that the older data were in remarkably good agreement with the new measurements,[55] and few of the determinations deviated more than one part in five hundred. The latest estimates of the latent heats below 50° by our colleagues impairs somewhat the earlier very striking agreement in this region, otherwise the accord is on the whole very good within the limits stated. Especially notable is the accord of Carlton-Sutton's value 2256.6 I. j.; Richards and Mathew's, 2256.5; Mathew's, 2255.2; and Henning's, 2255.7 with the present figure 2256.6. The only available determination at zero is apparently too low, the 2490.6 I. j. due to Dieterici.

Later important determinations of latent heats by our German Colleagues in the steam investigation, Jakob[56] and Jakob and Fritz[57] may be viewed as a continuation and extension of the earlier work of Henning, who, nearly thirty years ago, reached a temperature of 180°. The final comparison of these excellent results will be postponed to a later paper. The agreement of the computed latent heats with the new values is, however, quite satisfactory.

The Derived Enthalpy for Superheated Steam

During the course of the steam investigation preliminary experimental results for the enthalpy of superheated steam have been privately communicated by our English and Czechoslovakian colleagues. We have also had the privilege of seeing the results of Doctor W. Koch's computations of enthalpy based directly on his measurements of superheated steam. The latter data were particularly interesting because no assumed values of C_p° are involved, whereas equation (15A) depends directly upon the Gordon C_p° values. The general accord of the enthalpy computed from 15A with the experimental data and with Doctor Koch's deduced values is gratifying, and final comparisons must await full publication of the independent investigations, It may also be necessary finally to have further information on the magnitude of the differences in the international and thermodynamic temperature scales. Should the latter differences prove to be large it will be necessary to reformulate the equation of state for steam and recompute the derived quantities.

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[54] E. F. Fioch, Trans. Am. Soc. Mech. Eng., Fuels and Steam Power, *52*, 231 (1930).

[55] Osborne, Stimson and Fioch, U. S. Bur. Stand. J. Res. *5*, 411 (1930). Osborne, Stimson and Ginnings, Mech. Eng., *57*, 162 (1935).

[56] Max Jakob, Forschungsarbeiten Ver. Deutsch. Eng., *310*, 9 (1928).

[57] Max Jakob and W. Fritz, Zeit. Ver. Deutsch. Eng., *73*, 629 (1929).

TABLE XI

ENTHALPY VALUES FOR STEAM

p^{atm}	$p^{\frac{kg.}{cm^2}}$	100	150	200	250	300	350	400	450	500	550
1		(2675.35)	2776.22	2874.79	2973.43	3072.94	3173.67	3275.81	3379.48	3484.72	3591.58
	1	2675.80	2776.46	2874.94	2973.54	3073.02	3173.73	3275.86	3379.52	3484.76	3591.61
5			(2744.84)	2854.71	2959.95	3063.11	3166.10	3269.74	3374.48	3480.51	3587.97
	5			2855.58	2960.50	3063.51	3166.40	3270.14	3374.68	3480.68	3588.12
10				2826.07	2941.79	3050.26	3156.37	3262.04	3368.16	3475.21	3583.44
	10			2828.06	2944.01	3051.11	3157.00	3262.52	3368.57	3475.55	3583.74
25				(2790.46)	2877.66	3008.14	3125.45	3238.02	3348.74	3459.05	3569.70
	25				2881.51	3010.53	3127.17	3239.34	3349.80	3459.91	3570.43
50					(2799.00)	2921.77	3067.51	3194.99	3314.84	3431.26	3546.30
	50					2928.04	3071.51	3197.87	3317.08	3433.03	3547.83
100						(2747.05)	2918.67	3095.64	3240.77	3372.45	3497.70
	100						2930.01	3102.67	3245.80	3376.36	3500.80
150							2677.85	2971.96	3156.96	3309.40	3446.65
	150						2710.39	2985.28	3165.64	3315.21	3451.67
200							(2562.58)	2809.41	3060.81	3240.77	3393.09
	200							2833.55	3074.19	3249.86	3400.11
250								[2550.33]	2948.90	3166.89	3336.95
	250							[2607.05]	2968.32	3179.21	3346.15

[59] The values in parentheses are the values of enthalpy at saturation for the respective temperatures. The bracketed value under 400° corresponds to a volume less than 10 cc. per gram and is not considered on a par with the other values.

The results of the present computations of enthalpy are given in Table XI for even pressures in standard atmospheres and kilograms per cm.^{2} from 100° to 550°. In Table XII will be found the coefficients A, B, C and D of Equation 15A for pressures expressed in the two pressure units appearing in Table XI.

Some comparisons of the values of the enthalpy as given in Table XI with similar values from recent steam tables[58] are of interest.

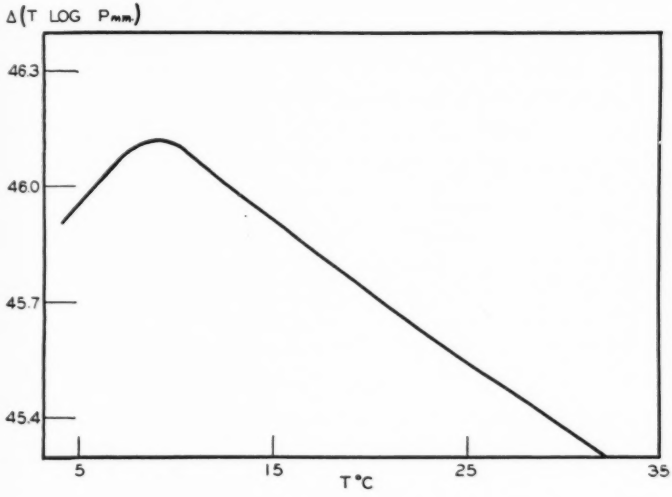

FIGURE 4

The following table, XIII, gives the differences in parts per thousand between the values of enthalpy in the latest steam tables of Knoblauch, Raisch, Hansen and Koch and those in Table XI. It is evident that the values in the latter table are increasingly smaller than the K. R. H. and K. values as higher pressures and higher temperatures are approached. The computed values are in better agreement with the Keenan steam table values as might be anticipated in view of the

[58] O. Knoblauch, E. Raisch, H. Hansen and W. Koch, Tabellen und Diagramme für Wasserdampf, Berlin, 1932. Herbert Moss, The Revised Callendar Steam Tables, London, 1931. Joseph H. Keenan, Steam Tables and Mollier Diagram, New York, 1930.

TABLE XII

VALUES OF THE COEFFICIENTS OF PRESSURE IN THE ENTHALPY EQUATION 15A

(All values are in Int. joules per gram of steam)

	−A	−B	−C	D	
100	12.5735	9.7886:−1	2.9957:− 3	negligible	atm.
	12.1691	9.1692:−1	2.6285:− 3	"	kg./cm.²
150	7.1061	2.3680:−1	2.0983:− 4	"	
	6.8776	2.2182:−1	1.8411:− 4	"	
200	4.5676	7.4531:−2	2.3550:− 5	6.5570:−19	
	4.4208	6.9814:−2	2.0664:− 5	4.2871:−19	
250	3.2024	2.8060:−2	3.5977:− 6	3.3255:−22	
	3.0994	2.6285:−2	3.1568:− 6	2.1742:−22	
300	2.3870	1.2001:−2	6.7363:− 7	4.1496:−25	
	2.3103	1.1242:−2	5.9107:− 7	2.7131:−25	
350	1.8608	5.6384:−3	1.4314:− 7	9.9183:−28	
	1.8009	5.2816:−3	1.2560:− 7	6.4847:−28	
400	1.5002	2.8435:−3	3.2161:− 8	3.1429:−30	
	1.4519	2.6635:−3	2.8219:− 8	2.0549:−30	
450	1.2412	1.5142:−3	6.9325:− 9	−1.3387:−32	
	1.2013	1.4184:−3	6.0829:− 9	−8.7526:−33	
500	1.0480	8.4112:−4	1.0959:− 9	−1.5184:−33	
	1.0143	7.8789:−4	9.6158:−10	−9.9275:−34	
550	0.8994	4.8282:−4	−1.2859:−10	negligible	
	0.8705	4.5225:−4	−1.1283:−10	"	

TABLE XIII

ENTHALPY DIFFERENCES BETWEEN THE 1932 KNOBLAUCH, RAISCH, HAUSEN AND KOCH STEAM TABLE VALUES AND THOSE OF TABLE XI

Differences are in parts per thousand and positive when the steam table values are the greater

°C	1 kg/cm.²	10	50	100	200	250
200	−1.10	−0.11				
300	−0.80	−0.75	+0.37			
400	−0.58	+0.18	+2.06	+3.27	+3.55	+3.42
500	−0.32	+0.92	+4.55	+6.25	+6.00	+6.07
550	−0.194	+1.20	+5.60	+8.05	+8.20	+7.10

fact that much of the data in the present steam papers was available for use at the time of their compilation. The Callendar-Moss values are larger than the computed, for example along the 400° isotherm by from 0.2 to 0.3 parts per thousand.

[50] The digits following the numbers are the indices of 10 forming the factors by which the numbers are to be multiplied. Thus the value of −B at 200° is 7.4531×10^{-2} or 0.074531.

In view of the expectation that the results of the extensive series of experimental determinations of enthalpy by our British, German and Czechoslovakian colleagues will be published in the near future, more extended comparisons with steam table values will not be presented here. It is of interest at this time to note that enthalpy values over the temperature range 0 to 550° and to pressures of 300 kg./cm.^{2} were adopted by the Third International Steam Tables Conference[61] held in the United States in September, 1934. The Table XI values are in accord with the conference values to the order of one per thousand or better over the range of temperature and to pressures including 250 kg./cm.^{2}

The Specific Heat Capacity of Superheated Steam

The heat capacity of steam for constant pressure may be very readily computed by means of an equation derived by differentiation from the enthalpy equation, 15A. The differentiation of the coefficients of the pressure was carried out directly for $\frac{\partial A}{\partial T}$ equal to $\tau\,(\beta - B_o)\,[0.20257 + 0.1886 \cdot 10^6\tau^2 + 0.014048 \cdot 10^{12}\tau^4]$ I. j. The derivatives of the coefficients B and C were obtained from a 10° interval table by using the Rutledge method already mentioned. In this instance three derivatives for each temperature were evaluated from the Rutledge coefficients and the average accepted as the true derivative desired. In the case of the D pressure coefficient its change with temperature is large and the differentiation operation was carried out on the logarithm of D. The Table XIV contains the coefficients of the C_p equation (I. j., kg./cm.^{2}) for each twenty degrees between 100° and 500° inclusive. The Table XV contains a few comparisons between the latest high pressure observed values of W. Koch[62] and those computed. An impression of the accord between all of the most recent specific heat measurements over the pressure range 30 kg.[63] to 200 kg. may be obtained from Fig. 5. It will be noted that the computed values for pressures of 120 kg. and lower pressures (+ points) lie systematically below the observed data to an increasing extent as the saturation line is approached. At 120 kg. there are two independent series of observations, the latest of which are smaller numerically than the earlier low pressure series. In the later series of measurements Dr. Koch modified his apparatus for the purpose of insuring the

[61] Mech. Eng., *57*, 701 (1935).
[62] W. Koch, Forschung auf dem Gebiete des Engenieurwesens, *3*, 1 (1932).
[63] Knoblauch and Koch, Zeit. Ver. Deutsch. Eng. *72*, 1733 (1928).

elimination of fog or liquid water particles in the steam. The possibility is not excluded that in the earlier measurements entrained water or fog was present which would be increasingly difficult to eliminate as observations were carried out nearer the saturation limit.

TABLE XIV

PRESSURE COEFFICIENTS OF THE EQUATION FOR THE CONSTANT PRESSURE SPECIFIC HEAT CAPACITY OF STEAM

$$C_p = C_p^\circ + A^1p + B^1p^2 + C^1p^4 - D^1p^{13}$$

kg./cm.², Int. j.

t	A'	B'	C'	$-D'$
100	1.5954:−1	2.921:−2		negligible
120	1.1093:−1	1.446:−2	4.596:− 5	"
140	7.979:−2	7.612:−3	1.492:− 5	"
160	5.907:−2	4.221:−3	5.306:− 6	"
180	4.483:−2	2.447:−3	2.035:− 6	"
200	3.477:−2	1.474:−3	8.320:− 7	"
220	2.748:−2	9.183:−4	3.595:− 7	2.812:−21
240	2.208:−2	5.890:−4	1.628:− 7	1.330:−22
260	1.801:−2	3.877:−4	7.683:− 8	7.416:−24
280	1.488:−2	2.611:−4	3.756:− 8	4.744:−25
300	1.244:−2	1.794:−4	1.892:− 8	3.431:−26
320	1.051:−2	1.255:−4	9.787:− 9	2.765:−27
340	8.967:−3	8.928:−5	5.175:− 9	2.449:−28
360	7.717:−3	6.444:−5	2.787:− 9	2.348:−29
380	6.693:−3	4.713:−5	1.524:− 9	2.387:−30
400	5.848:−3	3.489:−5	8.423:−10	2.485:−31
420	5.143:−3	2.612:−5	4.692:−10	2.451:−32
440	4.550:−3	1.974:−5	2.622:−10	1.637:−33
460	4.049:−3	1.506:−5	1.463:−10	−1.563:−34
480	3.622:−3	1.159:−5	8.087:−11	−1.226:−34
500	3.255:−3	8.794:−6	4.390:−11	−4.900:−35

The digit following the numbers are the indices of 10 forming the factors by which the numbers are to be multiplied. Thus the value of B' at 100 is 2.921×10^{-2} or 0.02921.

On the other hand it must not be overlooked that in the computations we are compelled to deal with second derivatives of volume with respect to temperature. Thus, even if it is admitted that the primary p, v, T data are exact and the selected empirical equation used appears satisfactory, it does not necessarily follow that derivatives obtained

by differentiation of the primitive equation will be exact. Of course the need for accurate derivatives was kept in view in working out the equation of state 9 and due care was exercised in the methods of obtaining the derivatives therefrom.

The importance of reliable specific heat measurements such as those of Knoblauch and Koch, and Koch is considerable for the measurements may be made the basis for a tabulation of thermody-

HEAT CAPACITY OF SUPERHEATED STEAM

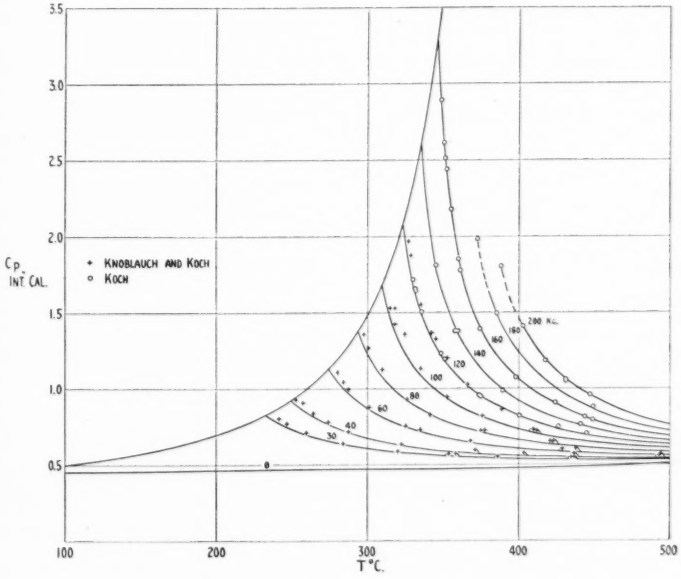

FIGURE 5

namic properties as has been pointed out by Koch. The data are also a severe test of the precision of p-v-T data and especially of the formulation used to represent volume data. The order of agreement of our computed specific heats with the observations, while not entirely within the limits of precision of the latest Koch measurements, is nevertheless a satisfactory indication that the equation of state 9 possesses no inherent defects when used within the limits specified.

The Entropy of Saturated and Superheated Steam

The general equation for the entropy is most conveniently derived from the differential equation $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ in view of the p, v, T data available. The limits of pressure are to be zero and finite pressures; of temperature, the ice point, T_o and T. We proceed with the integration as follows, adding and subtracting $R \log p$:[64]

$$S_1 = f(T) - R \log p + \int_o^p \left(\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)\right) dp + S_{o1}^\circ \qquad (24)$$

The quantity in brackets is zero where $\left(\frac{\partial v}{\partial T}\right)_p$ is given by $\frac{R}{p}$ as for the case $pv = RT$. Using the equation of state 9 and noting that $f(T)$ is given by $\int_{T_o}^{T} C_p^\circ \, d \log T$, we obtain for the S_1 equation:

$$S_1 = \int_{T_o}^{T} C_{p1}^\circ \, d \log T - 1.06242 \log_{10} p - \int_o^p \left(\frac{\partial B}{\partial T}\right)_p dp + S_1^\circ \qquad (24A)$$

The first integral we will evaluate using equation 22, resulting in the following expression:

$$\int_{T_o}^{T} C_{p1}^\circ \, d \log T = 3.38937 \log_{10} T/T_o + 7.5566 \cdot 10^{-4} (T - T_o) + 47.8365 (\tau_o - \tau) \qquad (25)$$

The evaluation of the remaining integral is facilitated once a table of B_o, φ_1, φ_3 and φ_{12} values and the pressure coefficients (Table XII) of the enthalpy equation 15A is compiled. The integral to be evaluated may be expressed as follows, using equation 5:

$$\int_o^p \left(\frac{\partial B}{\partial T}\right)_p dp = \frac{\partial B_o}{\partial T} p + \frac{1}{2}\frac{\partial \varphi_1}{\partial T} p^2 + \frac{1}{4}\frac{\partial \varphi_3}{\partial T} p^4 - \frac{1}{13}\frac{\partial \varphi_{12}}{\partial T} p^{13} = Kp + Lp^2 + Mp^4 - Np^{13} \qquad (26)$$

The coefficients A, B, C and D are equal respectively (Eq. 15) to $\frac{\partial B_o \tau}{\partial \tau}$, $\frac{1}{2}\frac{\partial \varphi_1 \tau}{\partial \tau}$, etc., whence it follows that $\frac{\partial B_o}{\partial T} = K = \tau\left(B_o - \frac{\partial B_o \tau}{\partial \tau}\right)$

[64] This device avoids an infinity which would otherwise appear in the integral.

TABLE XV

COMPUTED HEAT CAPACITIES COMPARED WITH THE RECENT MEASUREMENTS OF W. KOCH
UNITS INT. JOULES/G.

	120 kg./cm.²			140		160		180		200	
t	I	II	Comp.	obs.	comp.	obs.	comp.	obs.	comp.	obs.	comp.
340	5.926	5.788	5.708	8.969	8.948						
360	4.507	4.466	4.479	5.658	5.624	7.789	7.791				
380	3.846	3.813	3.836	4.449	4.501	5.386	5.420	6.818	6.864		
400	3.465	3.432	3.427	3.834	3.877	4.373	4.441	5.110	5.168	6.127	6.164
420	3.223	3.189	3.152	3.469	3.474	3.821	3.862	4.273	4.332	4.859	4.905
440	3.059	3.022	2.960	3.231	3.200	3.482	3.481	3.788	3.810	4.168	4.195
460	2.942	2.900	2.822	3.063	3.007	3.256	3.218	3.478	3.459	3.741	3.735

The column marked I is from the data of the investigation published in 1928 as given in Table I of the 1932 Steam Tables of Knoblauch, Raisch, Hausen and Koch. The column marked II is taken from Table 2 of W. Koch's paper of 1932.

with similar relations for L, M, and N, due attention being paid to the fractions $\frac{1}{2}$, $\frac{1}{4}$, and 1/13. Table XVI gives an abbreviated set of the coefficients valid for units kg. per cm.^{2}, int. joules per degree.

TABLE XVI

COEFFICIENTS OF PRESSURE FOR EQUATION 26

Int. j./deg.; kg.

t	K	L	M	$-N$
100	2.603−2	2.255−3	6.730− 6	
200	7.078−3	1.364−4	4.146− 8	8.944−22
300	2.965−3	1.765−5	9.790−10	4.670−28
400	1.570−3	3.556−6	4.016−11	3.018−33
500	9.601−4	9.182−7	1.222−12	1.258−36

The constant $S_1°$ is determined from a single value of S. That at 100° is conveniently taken from the work of Osborne, Stimson and Fioch at the National Bureau of Standards. The entropy of liquid water is given at 100° relative to 0° as 1.3059 joules per degree.[65] The entropy of evaporation at 100° from the same source is 6.04724 giving for the entropy of the saturated vapor at 100° (373.16) and 1.03323 kg./cm.^{2} the value 7.3536 int. joules per degree. From Table XVI we find $\int_0^{1\text{ atm.}} \frac{\partial B}{\partial T} d\rho$ to be 0.0293. The value of $\int_{T_0}^{T} C_{p1}° \, d \log T$ is 0.5817, and $S_1°$ becomes 6.8158 joules per degree K. The entropy at 0° C (ρ = 0.006226 kg.) may now be computed and is found to be 9.1577 joules per degree K. This number when multiplied by 273.16 gives 2501.52 I. j., a number which should be equal numerically to the heat of evaporation at zero. The number obtained from the enthalpy equation is 2501.86, a sufficiently satisfactory correspondence.

Table XVII contains a few values of the entropy for a range of temperatures and pressures computed from the equation 23A, using the equation 24, the coefficients of Table XVI and the constant 6.8163. The values from the Knoblauch, Raisch, Hausen and Koch steam tables have been entered in the table for comparison. Other values might also be entered for comparison but it is anticipated that in the near future a considerable body of new data will be reported and for this reason it seems best to postpone detailed intercomparison.

[65] This value as originally given is computed assuming T^0 to be 273.10 instead of 273.16. The number is therefore larger by about two units in the last place. The figure used has been communicated privately by Doctor Osborne.

The numerical values for other thermodynamic functions would be of interest, particularly the energy and the function $F = H - TS$. The latter can of course be easily computed from the values of H and S given in the present paper. In the case of the energy however it would be advantageous to represent the p-v-T data with pressure as the explicit variable thereby facilitating the computation of the term $\left(\frac{\partial p\tau}{\partial \tau}\right)_v$ of the energy equation:

$$U = \int_{T_o}^{T} C_v \, dT - \int_{o}^{p} \left(\frac{\partial p\tau}{\partial \tau}\right)_v dv + U^\circ \qquad (26)$$

In a later paper the equation of state in the form $p = f(vT)$ will be given and the energy of steam computed from an equation of the above form. Values of the energy can of course also be computed from the relation $H - pv = U$, using the data of the present paper.

TABLE XVII

ENTROPY OF STEAM

Calories per degree Kelvin*

	Kg./cm.²					
t	1	10	50	100	200	250
100	[1] 1.7603					
	[2] 1.7604					
200	[1] 1.8713	1.6005				
	[2] 1.8735	1.6011				
300	[1] 1.9627	1.7018	1.4859			
	[2] 1.9642	1.7036	1.4863			
400	[2] 2.0404	1.7841	1.5920	1.4910	1.3378	
	[2] 2.0421	1.7848	1.5903	1.4879	1.3335	
500	[2] 2.1100	1.8555	1.6730	1.5855	1.4790	1.4362
	[2] 2.1112	1.8553	1.6682	1.5789	1.4723	1.4307

THE JOULE-THOMSON COEFFICIENTS

A comprehensive investigation of the Joule-Thomson effect in steam was made by Davis and Kleinschmidt, comprising part of the 1921 A. S. M. E. program of steam research. Data were reported as

* Units are Int. joules/g. $\times \frac{1}{4.18605}$ or Int. steam calories per degree Kelvin.

[1] From the tables of Knoblauch, Raisch, Hausen and Koch.

[2] Computed from the entropy equation.

early as 1923.[66] The work was carried out for temperatures 125 to 400 inclusive, and for pressures extending to 40 kg./cm.^{2} The older results of similar measurements have been already critically discussed

TABLE XVIII

DAVIS AND KLEINSCHMIDT JOULE-THOMSON COEFFICIENTS COMPARED WITH COMPUTED VALUES

Units °C per Kg./cm.^{2}

p kg./cm.^{2}	D and K	Comp.	p kg./cm.^{2}	D and K	Comp.
	t = 125°			*t = 260°*	
1.125	4.801	4.908	1.60	1.485	1.495
	t = 145°		3.16	1.536	1.506
			10.55	1.549	1.539
1.405	3.730	3.928	14.77	1.548	1.548
2.81	3.998	4.009	15.11	1.577	1.549
	t = 166°		20.00	1.551	1.550
1.60	2.973	3.180	25.30	1.545	1.543
1.76	3.092	3.182	32.40	1.533	1.526
2.85	3.209	3.228	39.60	1.511	1.499
5.62	3.264	3.270			
	t = 196°			*t = 300°*	
1.60	2.368	2.405	1.70	1.163	1.168
3.52	2.409	2.451	3.16	1.193	1.174
7.04	2.557	2.500	8.44	1.192	1.188
7.04	2.474		14.00	1.207	1.199
7.60	2.522	2.505	15.00	1.197	1.199
10.55	2.570	2.500	20.25	1.201	1.202
10.55	2.490		32.70	1.187	1.199
	t = 225°			*t = 347°*	
1.60	1.882	1.910	1.60	0.932	0.905
3.16	1.995	1.930	7.38	0.929	0.918
7.04	1.978	1.970	15.00	0.928	0.922
10.55	1.948	1.985	35.00	0.919	0.926
14.77	1.987	1.990			
20.25	1.953	1.970			
20.25	2.001				

[66] R. V. Kleinschmidt, Mech. Eng. *45*, 165 (1923). H. N. Davis, Mech. Eng. *45*, 85 (1924); *47*, 107 (1925). J. H. Keenan, Mech. Eng. *48*, 144 (1926). R. V. Kleinschmidt, Mech. Eng. *48*, 155 (1926). H. N. Davis and J. H. Keenan, No. 455, World Eng. Conference Reports, Tokyo, 1929.

by H. N. Davis.[67] The first attempt to compute Joule-Thomson coefficients from the present volume data was published recently[68]

JOULE-THOMSON EFFECT VALUES
— = COMPUTED; O = OBSERVED

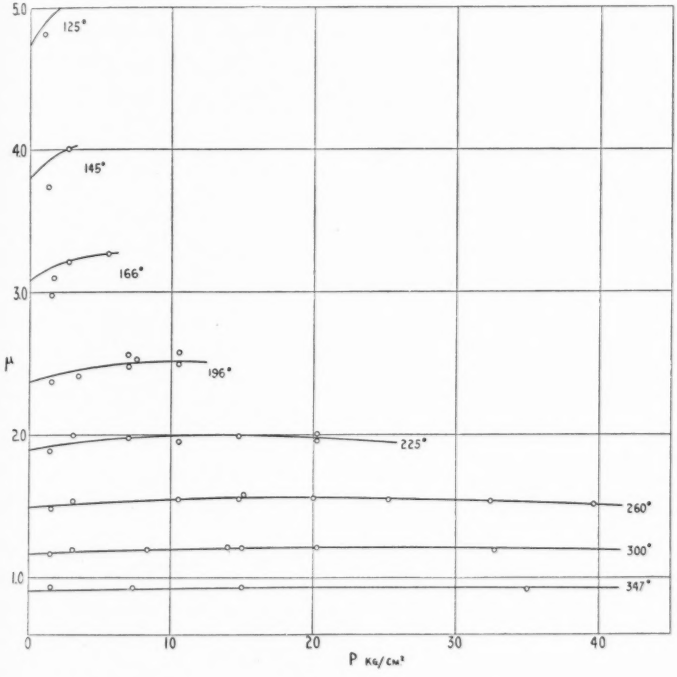

FIGURE 6

using for C_p° a relation deduced from a reduction of the recent enthalpy, specific heat and Joule-Thomson data referred to above. In the later paper a modification of the equation of state proposed to

[67] H. N. Davis, Proc. Am. Acad. Arts and Sci. *44*, (1909). See also Proc. Am. Soc. Mech. Eng. *30*, 1419 (1908).

[68] Keyes, Smith and Gerry, Mech. Eng. *57*, 113 (1934); also Mech. Eng. *59*, 164 (1935).

represent the present volume data to 10 cc. per gram was reported and a diagram given showing the agreement of new computations with the Davis and Kleinschmidt results. In these computations Gordon's C_p° values were used as given by Eq. 22.

The coefficients may readily be computed from the equation for enthalpy, 14, by differentiation resulting in the following equation:

$$\mu = \left(\frac{dT}{dp}\right)_H = -\frac{\left(\frac{\partial B\tau}{\partial \tau}\right)_p}{C_p^\circ + \partial/\partial T\left(\int \frac{\partial B\tau}{\partial \tau}\, dp\right)}$$

Tables XII and XIV give the data from which the Joule-Thomson numbers may be computed for the temperatures listed. Table XVIII gives for comparison the observed data under columns D and K and the computed Joule-Thomson values under the columns labelled "comp." The accord of the computations with the observations appears quite satisfactory but from figure 6 it is clear that the calculation does not reproduce the low pressure point at 125, 145, and the two low pressure points of the 166 isotherm. Aside from these defects, the accord with the observations appears to be everything that could be expected. The effect provides exceptionally good data for testing the equation of state, and the discrepancies noted may be an indication of a failure of the equation to give accurate results below 190°. Further information on this point will be forthcoming when the results of additional direct measurements of $\left(\frac{\partial H}{\partial p}\right)_T$ and μ are available using the new calorimeter referred to earlier (Part 1, reference 38). The new measurements will also supply information on the heat capacity of steam since this quantity is equal to the ratio of the isothermal increase of H with pressure to the Joule-Thomson effect.

NOTE: A most important paper by Max Jacob and W. Fritz appeared in Physikalische Zeitschrift, *36*, 651, 1935, containing a full report of their measurements on the physical properties of steam. This work appeared after the present paper had been sent in for publication. A comparison of the Jacob and Fritz work with the present results will be made in a later paper on the properties of steam.